



UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of : **Confirmation No. 8121**
Kazuyuki NITTA et al. : Docket No. 2001-1143A
Serial No. 09/928,430 : Group Art Unit 1752
Filed August 14, 2001 : Examiner S. Lee

POSITIVE-WORKING PHOTORESIST
COMPOSITION AND RESIST
PATTERNING METHOD USING SAME

DECLARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, the undersigned Kazuyuki NITTA, do hereby declare:

THAT I am an employee of Tokyo Ohka Kogyo Co., Ltd., Japan, the assignee of the above-identified United States patent application, since April, 1990, being engaged in the research and development works relative to the chemical-amplification positive-working photoresist compositions and other related products of the company;

THAT, I am one of the joint inventors in the above-identified pending United States patent application, I have full acquaintance with the subject matter of the above-identified pending application and have caused the comparative experiments described below either by myself or under my direct supervision; and

THAT I have a good knowledge of the English language and have read and understood the application papers and the prosecution history of the application.

COMPARATIVE EXPERIMENTS

I. Object of experiments

The comparative experiments below describe the results of the experiments conducted with an object to demonstrate the unexpectedly distinctive results obtained with the photoresist composition according to claim 1 after the separately proposed amendment, in which the polyvinyl ether compound as the component (C) is limited to an alicyclic polyvinyl ether compound such as 1,4-cyclohexanedimethanol divinyl ether, as compared with a similar photoresist composition but formulated with a linear aliphatic polyvinyl ether compound as the component (C).

II. Experimental procedures and results

Experiment 1 (inventive).

A positive-working photoresist composition was prepared by uniformly dissolving, in 670 parts by weight of propyleneglycol monomethyl ether, 75 parts by weight of a first polyhydroxystyrene resin having a weight-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 39% of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups, 25 parts by weight of a second polyhydroxystyrene resin having a weight-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 36% of the hydroxyl groups were substituted for the hydrogen atoms by *tert*-butoxycarbonyl groups, 5 parts by weight of bis(cyclohexylsulfonyl) diazomethane,

5 parts by weight of 1,4-cyclohexanedimethanol divinyl ether,
0.14 part by weight of salicylic acid and
0.1 part by weight of triethylamine
followed by filtration through a membrane filter of 0.2 μm pore
diameter.

A semiconductor silicon wafer provided on one surface with
a 0.12 μm thick anti-reflection coating film of an anti-
reflection coating agent (SWK-EX2, a product by Tokyo Ohka Kogyo
Co.) was coated with the photoresist composition obtained above
by using a spinner followed by heating on a hot plate at 90 °C
for 90 seconds to form a dried photoresist layer having a
thickness of 0.49 μm . The photoresist layer was exposed
pattern-wise to KrF excimer laser beams through a pattern-
bearing photomask on a minifying projection exposure machine
(Model NSR-S203B, manufactured by Nikon Co.) in an exposure dose
increased stepwise in an increment of 1 mJ/cm² followed by a
post-exposure baking treatment at 110 °C for 90 seconds and then
by a development treatment at 23 °C for 60 seconds with a 2.38%
aqueous solution of tetramethylammonium hydroxide followed by
rinse with water for 30 seconds and drying to give a resist
layer with a contact hole pattern of 0.19 μm .

The critical resolution was examined on the patterned
resist layer with the contact hole pattern obtained in the above
to find 0.17 μm .

The patterned resist layer obtained in the above was heated
at 135 °C to cause thermal flow which was examined for the
contact hole pattern of 0.19 μm diameter and the flow rate, i.e.
changes in the pattern size per °C, was measured in nm/°C and
recorded in three ratings of: A for a rate not exceeding 5
nm/°C; B for a rate of 5 to 15 nm/°C; and C for a rate exceeding
15 nm/°C.

The thermal flow rate for the patterned resist layer in
this experiment was 5.0 nm/°C and thus the thermal flow behavior
was rated as A. SEM photographs taken of the contact hole
pattern before and after the thermal flow treatment are attached
hereto as EXHIBIT.

Experiment 2 (comparative)

The experimental procedure was just the same as in Experiment 1 described above excepting for the replacement of 5 parts by weight of 1,4-cyclohexanedimethanol divinyl ether in the formulation of the photoresist composition with the same amount of 1,6-hexanediol divinyl ether.

The critical resolution was examined on the patterned resist layer with the contact hole pattern obtained in the above to find 0.18 μm .

The thermal flow rate for the patterned resist layer in this experiment was 12.4 nm/ $^{\circ}\text{C}$ and thus the thermal flow behavior was rated as B. SEM photographs taken of the contact hole pattern before and after the thermal flow treatment are attached hereto as EXHIBIT.

Experiment 3 (comparative)

The experimental procedure was just the same as in Experiment 1 described above excepting for the replacement of 5 parts by weight of 1,4-cyclohexanedimethanol divinyl ether in the formulation of the photoresist composition with the same amount of diethyleneglycol divinyl ether.

The critical resolution was examined on the patterned resist layer with the contact hole pattern obtained in the above to find 0.18 μm .

The thermal flow rate for the patterned resist layer in this experiment could not be obtained since a hole pattern had been closed due to too early thermal flow and thus the thermal flow behavior was rated as C. SEM photographs taken of the contact hole pattern before and after the thermal flow treatment are attached hereto as EXHIBIT.

III. Conclusion

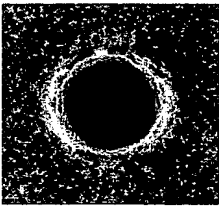
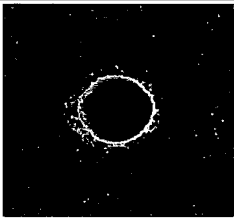
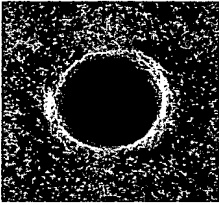
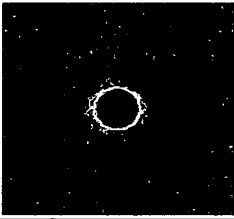
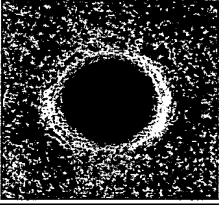
As is clearly understood from comparison of the above-described results of the inventive and comparative experiments, remarkable improvements can be obtained in the thermal flow

behavior as well as the critical pattern resolution by using 1,4-cyclohexanedimethanol divinyl ether as the component (C) in the formulation of the inventive photoresist composition as compared with the photoresist compositions in Experiments 2 and 3 formulated with a linear aliphatic divinyl ether compound.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of any application or any patent issued thereon.

Date: March 29, 2004

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	Before thermal flow treatment	After thermal flow treatment
Experiment 1		
Contact hole diameter	190 nm	140 nm
Experiment 2		
Contact hole diameter	190 nm	66 nm
Experiment 3		No hole pattern
Contact hole diameter	190 nm	

EXHIBIT

